PHASE FORMATION IN CERAMIC MIXTURES CONTAINING METADIABASE

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The processes of mullitization of high-temperature ceramic mixtures containing metadiabase are investigated. The quantitative relationship between mullite, quartz, and plagioclase is demonstrated. It is established that the introduction of 30 wt.% metadiabase at firing temperatures of 1180 – 1200°C accelerates the mullitization process and facilitates the formation of mullite with a more perfect structure. Mullite in ceramic mixtures is mostly crystallized from the kaolinite residue, as well as from plagioclase grains.

Mullite is the crystalline phase which to a large extent determines the properties of the finished ceramic product. The chemical resistance and physicomechanical and service parameters of ceramics qualitatively depend on the mullite structure. For example, the acid resistance of mullite with a perfect structure is 98 – 99%, whereas mullite with an imperfect structure is not acid-resistant [1]. According to the data in [2], the structure of mullite has an effect on the thermal resistance of products.

The purpose of the present investigation was to study the mullite formation process in ceramic mixtures containing metadiabase as a flux.

The investigation was carried out in the system of sections (here and elsewhere content in mass % is indicated): 0 – 40 kaolin, 50 high-melting clay, 10 – 50 metadiabase; and 30 – 70 kaolin, 10 – 50 clay, 20 metadiabase. The selected initial materials included Glushkovichskoe deposit kaolin (Belarus), Vesko-Granitik clay from the Veselovskoe deposit (Ukraine), and Mikashevichskii diabases (Belarus).

Glushkovichskii kaolin (Lel'chitskii district) is a low-plastic or, less frequently, moderately plastic (plasticity number of 6 – 16) material, little sensitive to drying. Kaolin is a disperse and coarse-disperse material with a high sand impurity content and refractoriness of 1650 – 1750°C. Its mineralogical composition is represented by kaolinite and quartz [3].

The diabases (Zhitkovichskii district) are the effluent compact massive rocks which consist mostly of minerals of the amphibole and plagioclase groups, as well as biotite. According to SiO_2 content, they are classified as base rocks and have an increased content of pigment oxides (around 15%) as well as oxides of alkaline and alkaline-earth metals. The overall content of the latter comprises 22 – 25%. The presence of up to 19% aluminum oxide is a valuable property.

The variety of these rocks used in the experiments consisted of fine-grained and close-grained metadiabase [4].

Data on the Veselovskoe deposits clays are well described in the literature [5, 6].

The experimental mixtures were prepared using the standard method. Separate wet grinding of the components was carried out in a ball mill up to a residue of not more than 1% on a No.0063K sieve. The samples were compressed at a pressure of 35 – 40 MPa and fired at temperatures of 1100 – 1200°C with exposure in the maximum temperature range for 15 min.

According to the x-ray phase analysis data, the qualitative phase composition of the fired ceramic mixtures is represented mainly by mullite, quartz, hematite, wustite, and plagioclase. The closely related values of the interplanar distances do not allow for precise x-ray discrimination of the minerals which belong to the plagioclase group; therefore, the above listed minerals in fired samples of the mixtures based on metadiabase will henceforth be designated by the term "plagioclase."

Analysis of the diffraction maximum intensities of the main crystalline phases versus the metadiabase content at various firing temperatures (Fig. 1) reveals a certain relationship between the quantity of the emerging mullite and the dissolved quartz.

As the metadiabase content in mixtures increases, all fired samples exhibit a decrease in the intensity of the quartz diffraction maxima in their diffraction patterns. This is especially perceptible at a firing temperature of 1200°C (Fig. 1b): with increasing metadiabase content from 10 to 40%, the intensity of the peaks corresponding to quartz decreases virtually to one-fourth. This is due to the dissolution of quartz in the ferrous-silicate melt which is intensely formed within a temperature range of 1150 – 1200°C

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and whose quantity increases as the metadiabase content increases.

As the amount of quartz in the system within the considered temperature interval decreases, the content of mullite is reduced, although insignificantly. Obviously, as the melt is saturated with a high amount of SiO_2 in the course of quartz dissolution, a liquid phase is formed with an increased capacity for dissolving mullite. This process is especially perceptible at firing temperatures up to 1150°C, when the mullite is formed mainly from the kaolinite component of ceramic mixtures [4].

Samples fired at a temperature of 1200°C apparently show a certain relationship between the crystallization processes of mullite and plagioclase. In ceramic mixtures containing between 10 and 20% metadiabase, the quantity of mullite estimated by the intensity of the diffraction maxima decreases slightly, with 30% metadiabase content it grows, and with 40% content it decreases again. The variations in the quantity of plagioclase at this temperature are reversible.

It should be noted that articles fired at temperature of 1100 – 1150°C and containing a substantial amount of metadiabase (30 – 60%) exhibit high deformation resistance. The dissolution of quartz and, consequently, the saturation of the liquid phase by compound anion complexes $Si_xO_y^{-2}$ are presumably responsible for the monotonic decrease in the mixture viscosity, which, in turn, contributes to an increase in the deformation resistance of the article.

At a temperature of 1200°C, intense dissolution of both initial and crystalline phases formed upon firing is observed in samples containing 40% of metadiabase. Fired specimens became almost x-ray-amorphous after indroduction of 50% of metadiabases.

Analysis of the phase content of the specimens as a function of the amount of introduced kaolin at a constant content of metadiabases (20%) showed that at a firing temperature of 1150°C the amount of quartz and mullite gradually grows as the content of sandy Glushkovichskii kaolin inctreases and the plagioclase and hematite content remain the same.

At a temperature of 1200°C, the intensity of the peaks corresponding to quartz decreases, and that of mullite grows. The mullitization process at the specified temperature is largely determined by the quantity of the plagioclase present in the system. The quantity of mullite virtually does not vary in the samples containing 40 and 50% kaolin in which the complete amorphization of plagioclase is observed.

A more detailed study of the mullitization process and of the mullite structure was carried out using x-ray phase analysis based on the variation in the reflection intensity of the mullite diffraction maxima corresponding to the face indexes hkl (110), (210), and (120), in accordance with the known methods [7, 8].

At a firing temperature of 1100°C, the peak area corresponding to an interplanar distance of 0.54 nm and the index value hkl (110) is approximately equal in all samples (the difference is within the experimental error). At this temperature, seeds of mullite crystals are formed in the samples. When the temperature increases from 1150°C to 1180°C, the
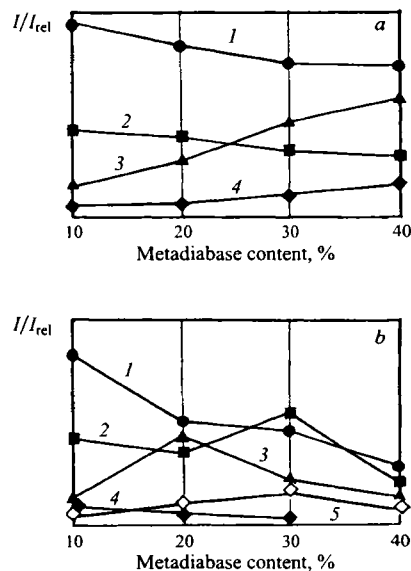

Fig. 1. Diffraction maxima intensities of the main crystalline phases versus the metadiabase content at a firing temperature of 1150 (a) and 1200°C (b): 1) quartz; 2) mullite; 3) plagioclase; 4) hematite; 5) wustite

amount of mullite in the samples containing 10 and 20% metadiabase sharply increases. All peak parameters vary jumpwise. Thus, the peak area at a temperature of 1150°C compared to a temperature of 1100°C is nearly 4 times larger. Therefore, it can be inferred that the mullite content increases in the same proportion. The jumpwise increase in the quantity of the released mullite coincides with the almost complete amorphization of plagioclase. In the samples containing 20% metadiabase, this occurs at the temperature of 1180 – 1200°C.

At a firing temperatures of 1180 – 1200°C, the peak area decreases slightly. Apparently, the dissolution of the primary mullite and the crystallization of the secondary mullite, which has a more perfect crystalline structure, occur within this temperature interval.

With increase in heating temperature starting at 1150°C, the peak area corresponding to an interplanar distance of 0.54 nm in the diffraction patterns of the samples containing 30% metadiabase virtually does not vary, but the peak intensity and integral width change. The vertical drawing and simultaneous horizontal narrowing can be accounted for by the disappearance of distortions in the crystalline lattice of the mullite and the possible growth of crystals.

The dissolution of mullite crystals in samples containing 40% metadiabase is observed at a firing temperature of 1200°C and higher.

The nature and degree of resolution of the diffraction maximum reflections corresponding to the plane indexes (120) and (210) can be found from the data in Table 1 and Fig. 2. It can be seen in Table 1 that the ratios of reflection intensities (120) and (210), as well as the ratios of the depth of the band R dividing the specified reflections to their inten-
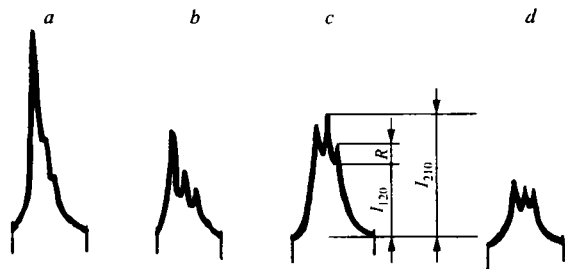
Fig. 2. Degree of resolution of reflections (120) and (210) of samples containing 10% (a), 20% (b), 30% (c) and 40% (d) metadiabase fired at the temperature of 1200°C.

sity in the ceramic samples of model compositions, are significantly different.

The analysis of the given data established the following regularities. The ratios R/I_{210} and R/I_{120} in the samples fired at a temperature of 1200°C increase with an increase in the content of the ceramic mixture components: in the first case, metadiabase (with a constant content of the clay component), and in the second case, kaolin (Fig. 2), which is presumably related to the perfection of the mullite crystal lattice.

Apparently, Fe^{2+} and Fe^{3+} ions are capable of incorporating into the mullite lattice and forming anion vacancies which have a special significance for the synthesis of mullite, since they increase the number of defects and thus accelerate the mullite crystallization.

According to the data in [9], the depth of the bands dividing the plane reflections (120) and (210) in aluminosilicates increases as the mullite phase in transformed to mullite: from the composition $2Al_2O_3 \cdot SiO_2$ to the composition $3Al_2O_3 \cdot 2SiO_2$.

By determining the mechanical strength and acid resistance of the fired samples, we established that as the firing temperature increases, mullite with a more perfect structure

TABLE 1

Batch composition of mixtures*, %	Ratio of the dividing band depth to the intensity of mullite diffraction maximum		
	I_{210}/I_{120}	R/I_{210}	R/I_{120}
40 kaolin, 50 clay, 10 metadiabase	1.78	0.023	0.042
30 kaolin, 50 clay, 20 metadiabase	1.57	0.090	0.140
20 kaolin, 50 clay, 30 metadiabase	1.40	0.045	0.067
10 kaolin, 50 clay, 40 metadiabase	1.05	0.220	0.230
40 kaolin, 40 clay, 20 metadiabase	1.37	0.037	0.050
50 kaolin, 30 clay, 20 metadiabase	1.46	0.050	0.076
60 kaolin, 20 clay, 20 metadiabase	1.53	0.075	0.120

* Firing at a temperature of 1200°C.

is formed and its content in the samples fired at 1150 and 1180°C increases; therefore, the acid resistance of the articles with respect to 1 normal HCl solution increases from 86 to 95%, respectively, and the mechanical strength grows from 32 to 38 – 42 MPa.

Study of the microstructure of the synthesized samples using the electron microscope revealed that mullite crystals are impossible to identify and discriminate in samples fired at temperatures below 1100°C. At higher temperatures (over 1100°C), mullite crystals are clearly visible.

Electron microscope photographs of the samples fired at 1100°C (Fig. 3a) exhibit structural elements mostly represented by the aggregates of amorphized argillaceous components and quartz and mullite crystals. Mullite is represented either by crystal seeds 0.04 – 0.12 μm long, or by short columnar crystals of almost square section up to 0.1 μm long.

At a temperature of 1150°C, the mullite crystals (Fig. 3b) are characterized by a zonal structure, and the number of zones ranges from 2 to 5. The smaller the size of the zonal crystals, the more frequently they are observed. With increasing temperature and with growth of the crystals, the zonal structure gradually disappears (1200°C). An increase in the temperature not only results in the disappearance of the crystal zonality, but modifies the crystal symmetry as well: they change to a prismatic morphological variety. At the temperature of 1200°C, the difference in the morphology of the mullite crystals is more clearly visible in the structure of the material. Short columnal seed crystals, as well as prismatic crystals up to 0.6 – 0.7 μm long, can be seen. The ratio between the sizes of the long and short prismatic axes in this case tends to increase, and comprises 1 : 5 – 1 : 14 at a firing temperature of 1150°C.

The most intense crystallization at the temperature of 1150°C is observed at the interface of the amorphized argillaceous material and glass. This type of mullite crystallization points to an obvious effect of the fluxes (iron oxides, alkaline metal oxides) on the process. Fluxes facilitate the growth of the mullite crystals and perfect their structure.
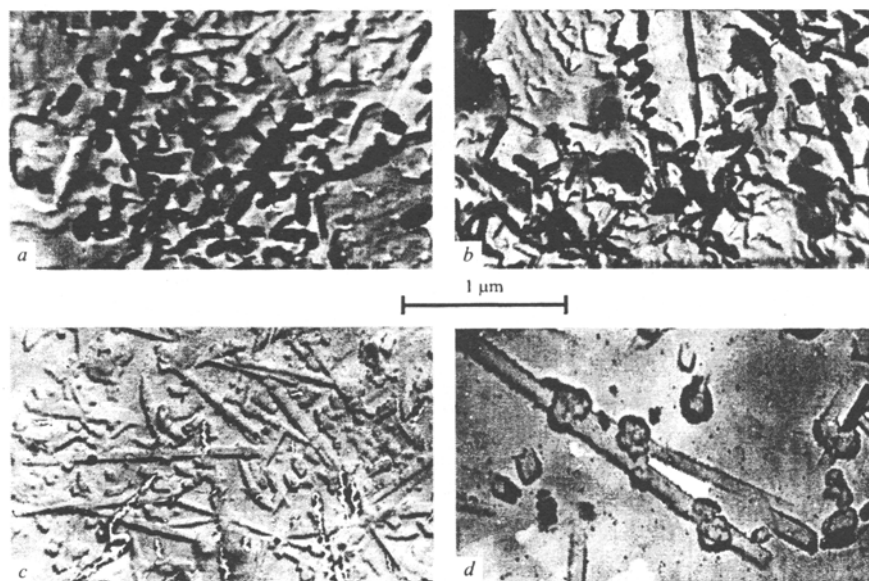
There is a inverse relationship between the amount of plagioclase and the forming mullite. As the content of the latter increases, the plagioclase content sharply decreases. Apparently, in this case the mullite is crystallized at the expense of plagioclase which passes into the melt. However, the phenomenon known in the literature as "glass pseudomorphosis and needle-shaped mullite" was not identified here.

The formation of the needle-shaped mullite variety from plagioclase is based on the process of alkaline metal diffusion [10]. By leaving the albite lattice, the alkaline metals free part of the charges, which strengthens the ionic bond of aluminum and leads to the formation of six coordination groups of this element needed for the mullite synthesis. Moreover, the decrease in the concentration of sodium ions in the plagioclase melt results in the formation of the matrix whose composition is shifted toward the mullite field in the phase diagram of the $R_2O – Al_2O_3 – SiO_2$ system. After diffusion of the alkaline metal oxides, a certain oxide concentration of the R_2O type is attained in the "kaolinite residue," on

Fig. 3. Electron microscope photographs of samples fired at temperatures of 1100 (*a*), 1150 (*b*), 1200 (*c*), and 1200°C (*d*) with the metadiabase content in the mixtures equal to 20% (*a − c*) and 30% (*d*).

which basis the liquid phase is formed. Its composition is constantly modified due to the penetration of new portions of alkalis and due to the dissolution of quartz, which also contributes to mullite recrystallization and perfection of its structure.

Study of the microstructure of the samples fired at a temperature of 1200°C (Fig. 3*c*, *d*) indicated that the emerging mullite crystals predominantly have prismatic and needle shapes. Their size ranges from 0.5 to 4.0 μm, depending on the initial mixture composition. The mullite prevailing at the specified temperature by its morphological parameters is attributed to secondary mullite. The formation of secondary mullite is especially typical of ceramic mixture samples containing over 20% metadiabase.

It can be seen in Fig. 3 that the formation of mullite with a more perfect structure proceeds both through better defined crystal edging, and through the formation of crystals with a more clearly defined symmetry.

Certain formations in the form of infinitesimal spheroid drops whose sizes are 0.05 − 010 μm can be identified in the vitreous phase of the samples (Fig. 3*d*) containing 30% metadiabase and fired at a temperature of 1200°C. The observed liquation of the vitreous phase presumably contributes to the crystallization of secondary mullite in ceramic mixtures containing metadiabase.

Thus, when nonconcentrated kaolin and metadiabase are introduced to a ceramic mixture composition, the character of their effect on the mullitization process is determined by the initial mineralogical composition of the rock-forming minerals and their chemical composition. The oxides (FeO, Fe_2O_3, and Na_2O) have a mineralizing effect and contribute to the formation of a more perfect structure in the emerging mullite, especially at relatively low firing temperatures (1150 − 1200). Introduction of metadiabase contributes to the formation of the ceramic crock phase composition which is mostly represented by mullite, quartz, and plagioclase. Their

favorable combination together with the vitreous phase provide for sufficiently high technical properties of the products.

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